Water analysis by X-ray fluorescence spectrometry using UltraCarry

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1. Liquid Analysis by X-ray Fluorescence Spectrometry

X-ray fluorescence (XRF) analysis has a wide range of applications because it allows quick and non-destructive qualitative and quantitative analysis of contained elements with simple sample preprocessing and has excellent measurement reproducibility. It is used in the industrial fields of steel, non-ferrous metals, mining, petroleum, ceramics, cement, and for R & D and quality control of electronic materials such as multilayer capacitors and piezoelectric elements(1).

In the environmental analysis field, XRF analysis is mainly used for hazardous element analysis, and is applied to screening analysis of restricted substances according to the RoHS(2) directive and contaminated soil(3). XRF analysis is environmentally friendly because it does not produce waste liquid unlike ICP and ICP-MS analysis, both official methods for water analysis. Therefore, the application of XRF analysis to water quality management of industrial wastewater, agricultural water, springs, rivers, lakes is expected to increase.

Figure 1 shows XRF liquid analysis methods. The method in Fig. 1(a) utilizes a liquid sample cell, which enables measurement of a liquid sample as-is, in a sample chamber filled with helium or nitrogen. In (b) and (c), the droplet method is used, in which a liquid dropped on a filter paper is dried to remove the solvent and then measured under vacuum. The lower limits of detection of analytical method (b) using MicroCarry, are ppm-level. This is not sufficient for environmental analysis, which requires ppb-level sensitivity. UltraCarry(4), (5) high-sensitivity droplet filter paper, which is described in this article, was developed to meet that demand. It enables XRF analysis with a ppb-level lower limit of detection. The analyzable concentration range of each method is shown in Fig. 1(d).

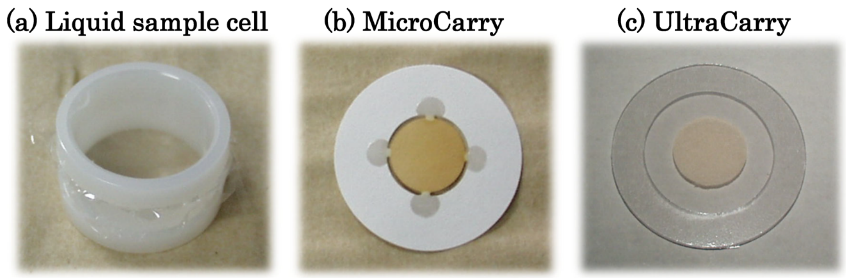
2. Principle and Property of UltraCarry

Lower limit of detection (LLD) is defined by the following equation;

$$LLD = 3 \times a \times \sigma_{BG}$$

a: calibration slope,
σ_{BG}: statistical error of background intensity

To improve the detection limit, it is necessary to (1)



(d) Lower limits of detection for each method

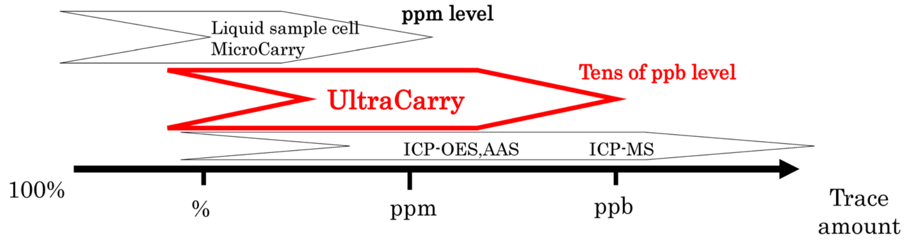


Fig. 1. Liquid analysis methods and lower limits of detection of (a) liquid sample cell, (b) MicroCarry (filter paper), (c) UltraCarry (high-sensitivity filter paper).

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improve sensitivity (which decreases the value of slope a) and/or (2) reduce the background (which decreases the value of statistical error σ_{BG}).

Figure 2 shows schematic diagrams of the principles of the measurement method using MicroCarry and UltraCarry. With the conventional droplet filter paper MicroCarry, high fluorescent X-ray intensity cannot be obtained because the liquid retaining capacity of the filter paper is small, as shown in Fig. 2(a). During the measurement, a large amount of scattered X-rays are generated from the filter paper, causing high background intensity. Consequently, the lower limit of detection is at the same level as that of the ordinary liquid analysis method.

On the other hand, UltraCarry, shown in Fig. 2(b), has thin special paper with high element adsorptive property attached to a thin polymer film. Since the special paper is hydrophilic and the surrounding polymer film is hydrophobic, a large amount of liquid can be dropped on the special paper in part due to the surface tension properties of water. Since the dried sample residue on UltraCarry is highly concentrated, high fluorescent X-ray intensity can be obtained.

Moreover, since the polymer film and the special paper are thin, the background intensity due to scattered X-rays is greatly reduced, drastically improving the lower limit of detection (LLD).

Figure 3 shows the analysis results of the same sample using UltraCarry, MicroCarry, and a liquid sample cell. The measured sample was a multielement standard solution supplied by Spex Certiprep, Inc. (10 ppm for each element). A ZSX Primus IV wavelength dispersive X-ray fluorescence spectrometer was used. The tube voltage and current condition was 50 kV−48 mA.

The qualitative spectrum (green line) obtained using the liquid sample cell in Fig. 3(a) shows that the background intensities due to the liquid are high and trace element analysis is difficult. The red line is the measurement result using MicroCarry, and the amount of dropped solution was $100\,\mu$L. The peak of each element of 10 ppm can be slightly observed. The blue line in Fig. 3(c) is a qualitative spectrum obtained using UltraCarry, and the amount of dropped solution was

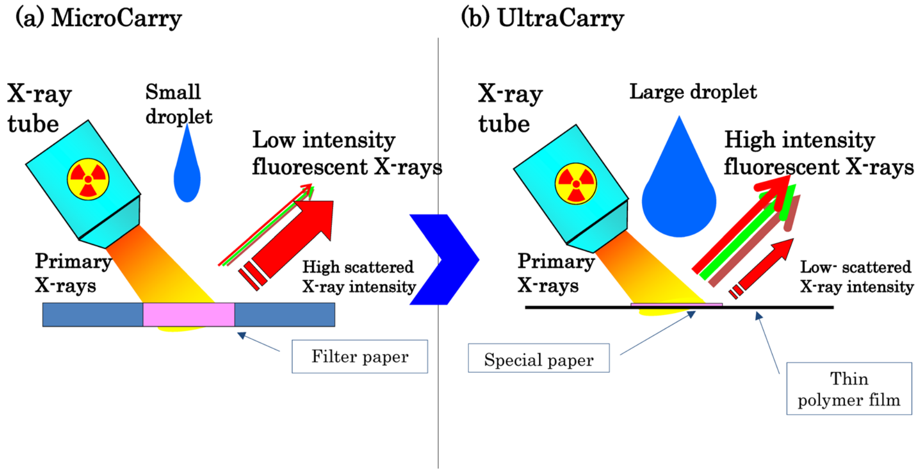


Fig. 2. Schematic diagrams for the droplet methods.
(a) MicroCarry, (b) UltraCarry.

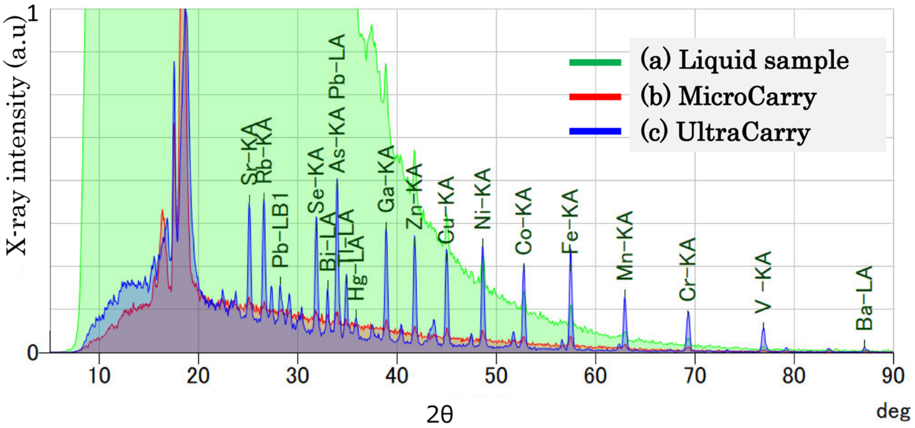
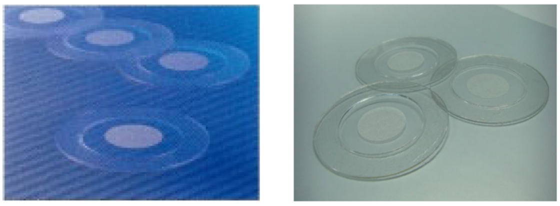


Fig. 3. (a) Green line: liquid sample cell, (b) red line: MicroCarry, (c) blue line: UltraCarry.
Tube voltage-tube and current: 50 kV−48 mA.
Sample: XSTC-13B, a general-purpose multi-element standard solution from SPEX (10 ppm for each element).

500 μL. High peak–to-background ratios were obtained with clear peaks, which indicates that UltraCarry enables highly sensitive analysis.

There are two types of UltraCarry, depending on the application. UltraCarry (Fig. 4(a)) was developed for environmental analysis and supports analyses of heavy elements including hazardous elements and some light elements. UltraCarry Light (Fig. 4(b)) supports analyses of heavy elements and a wider range of light elements, although the sensitivities for heavy elements are slightly lower than that of UltraCarry.

For the sample preparation, a liquid sample pipetted on an UltraCarry should be dried by air-drying or a dryer with blower. Since a polymer material is used for UltraCarry, drying at around 60°C is recommended. The dedicated vacuum dryer UltraDry(6) (Fig. 4(c)) allows filters to be dried quickly, reducing sample preparation time.



(a) UltraCarry

(b) UltraCarry Light

(c) UltraDry vacuum dryer

Fig. 4. (a) UltraCarry, for hazardous heavy elements and some light elements. Sample should be pipetted on the special paper in the center.
(b) UltraCarry Light, for a wide range of elements.
(c) UltraDry, the dedicated vacuum dryer. It can be used for vacuum drying and low-temperature heating. Drying time is about 30 minutes (depends on the number of samples).

Table 1 shows a list of lower limits of detection for UltraCarry. UltraCarry is an application tool that enables high-sensitivity analysis of aqueous solution, for cases where XRF analysis has insufficient sensitivity using conventional methods.

3. Quantitative Analysis of Mineral Components in Drinking Water of Mineral Water

As an application example, quantitative analyses of mineral components in some kinds of mineral water were performed. UltraCarry Light filter papers suitable for light element analysis were used.

Table 2 shows the measurement conditions for quantitative analysis. The thirteen elements from Na to Sr were analyzed. The standard samples for preparing the calibration curves came from a diluted standard solution for atomic absorption spectrophotometry. The dropping amount per specimen on UltraCarry was 500 μL.

Table 1. Lower limits of detection (LLD) for measurements with UltraCarry.

Unit: ppb

Elements	LLD	Elements	LLD
As	***16***	V	34
Pb	***76***	Mn	16
Cr	***26***	Ni	20
Se	***24***	Cu	19
F	***1 ppm***	Zn	18
B	***32 ppm***	Sr	25
Cd	***182***	Mo	27
Na	76	Ag	152
P	56	Ba	105
K	12	Tl	81

· LLDs were obtained from the SQX results (measurement time: 100 sec), except for F and B.
· LLDs for F and B were obtained from the results by the calibration curve method.
· Tube voltage–tube current was 50 kV–48 mA for heavy elements, 30 kV–100 mA for light elements.

Table 2. Measurement conditions of the quantitative analyses.

Measurement line	Na Kα	Mg Kα	Al Kα	Si Kα	P Kα	S Kα	Cl Kα	K Kα	Ca Kα	Cr Kα	Mn Kα	Fe Kα	Sr Kα
kV–mA	30–100	30–100	30–100	30–100	30–100	30–100	30–100	40–75	40–75	50–60	50–60	50–60	50–60
Filter	OUT	OUT	OUT	OUT	OUT	OUT	OUT	OUT	OUT	Al125	Al125	Al125	Ni
Attenuator	1/1	1/1	1/1	1/1	1/1	1/1	1/1	1/1	1/1	1/1	1/1	1/1	1/1
Slit	S4	S4	S4	S4	S4	S4	S2	S4	S4	S2	S2	S2	S2
Analyzing crystal	RX35	RX35	PETH	PETH	GeH	GeH	GeH	LiF (200)	LiF (200)	LiF (200)	LiF (200)	LiF (200)	LiF (200)
Detector	F-PC	F-PC	F-PC	F-PC	F-PC	F-PC	F-PC	F-PC	F-PC	SC	SC	SC	SC
Measurement time (sec)													
Peak	60	60	60	60	60	60	60	60	60	60	60	60	60
Background	30×2	30×2	30×2	30×2	30×2	30×2	30×2	30×2	30×2	30×2	30×2	30×2	30×2

· Measurement diameter: 30 mm
· Measurement atmosphere: vacuum
· Al sample supports (cup-type) were used for measurement. Ti sample support was used for Al analysis.

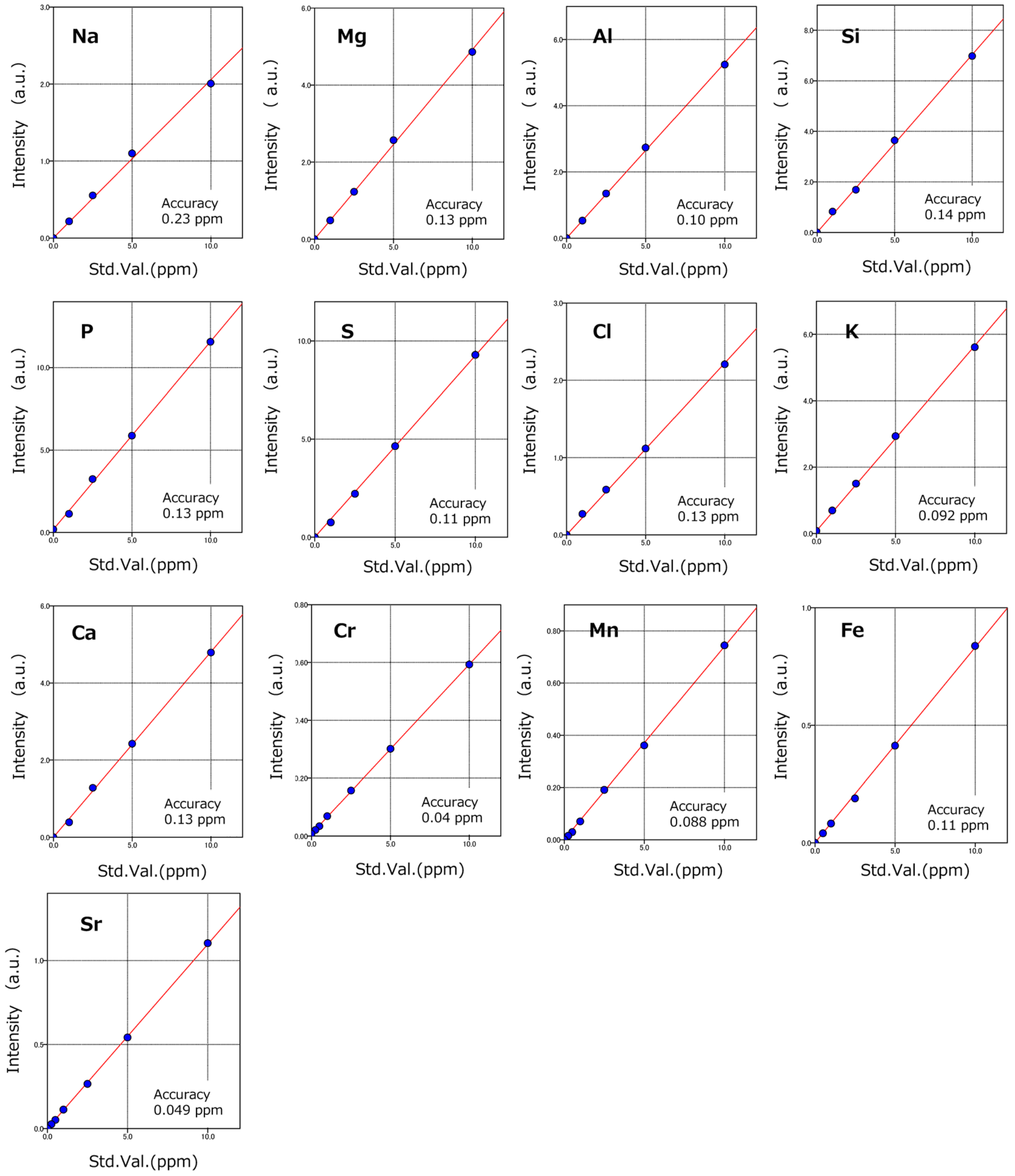


Fig. 5. Calibration curves.

Table 3. Lower limits of detection.

Unit: ppb

Component	Na	Mg	Al	Si	P	S	Cl
LLD	0.031	0.026	0.013	0.023	0.010	0.011	0.050
Component	K	Ca	Cr	Mn	Fe	Sr	
LLD	0.017	0.024	0.027	0.021	0.037	0.034	

Measurement times: 100 seconds for peaks, 50×2 seconds for backgrounds

Figure 5 shows the calibration curves for each element. They show good correlations. The LLDs obtained from these calibration curves are shown in Table 3. In the light element region, the LLDs are from ten to tens of ppb.

Commercial mineral waters from seven companies were analyzed using the calibration curves. Table 4 shows the results of the quantitative analyses. Approximate mineral element contents provided on the labels of each mineral water are shown below the quantitative analysis values in the table for reference. They show good agreement.

As the results above show, quantitative analysis with the calibration method using UltraCarry Light is a good method for the analysis of trace mineral element components in drinking water.

4. Screening Analysis Using SQX

Next, an example of screening analysis by SQX (Scan Quant X) is shown. SQX(7) is a standardless analysis using the FP method utilizing qualitative analysis results. The total measurement time was about 10 minutes, which is the same as the standard condition for the EZ scan. Figure 6 shows the qualitative analysis

Table 4. The quantitative analysis results.

Units: ppb

	Na	Mg	Al	Si	P	S	Cl	K	Ca	Cr	Mn	Fe	Sr
Company A	**34.9**	**21.8**	**0.095**	**20.7**	**n.d.**	**10.9**	**5.03**	**9.25**	**17.4**	**n.d.**	**n.d.**	**0.055**	**0.23**
Label value	30–65	6–15	—	9–20	—	5–20	3–10	3–15	10–120	—	—	—	0.2–0.5
Company B	**3.25**	**13.2**	**n.d.**	**4.03**	**n.d.**	**19.1**	**22.8**	**0.49**	**57.4**	**n.d.**	**n.d.**	**0.062**	**0.37**
Label value	3–16	4–39	—	—	—	—	—	0.12–5	18–96	—	—	—	0.5±0.3
Company C	**3.39**	**10.4**	**n.d.**	**13.1**	**0.12**	**1.38**	**1.85**	**3.39**	**8.54**	**n.d.**	**n.d.**	**n.d.**	**0.03**
Label value	—	>5	—	>6.5	—	—	—	>3.5	>40	—	—	—	—
Company D	**2.48**	**27.8**	**n.d.**	**6.47**	**n.d.**	**4.21**	**8.33**	**1.04**	**58.5**	**n.d.**	**n.d.**	**0.11**	**0.38**
Label value	6.5	26	—	7	—	4.2	6.8	1	80	—	—	—	0.4
Company E	**0.21**	**1.33**	**n.d.**	**0.98**	**n.d.**	**n.d.**	**0.13**	**0.11**	**n.d.**	**n.d.**	**n.d.**	**0.038**	**n.d.**
Label value	n/a												
Company F	**n.d.**	**1.50**	**n.d.**	**1.65**	**n.d.**	**n.d.**	**0.23**	**n.d.**	**n.d.**	**n.d.**	**n.d.**	**0.15**	**n.d.**
Label value	n/a												
Company G	**2.09**	**6.69**	**n.d.**	**6.61**	**n.d.**	**1.49**	**6.06**	**0.87**	**16.1**	**n.d.**	**n.d.**	**n.d.**	**0.11**
Label value	n/a												

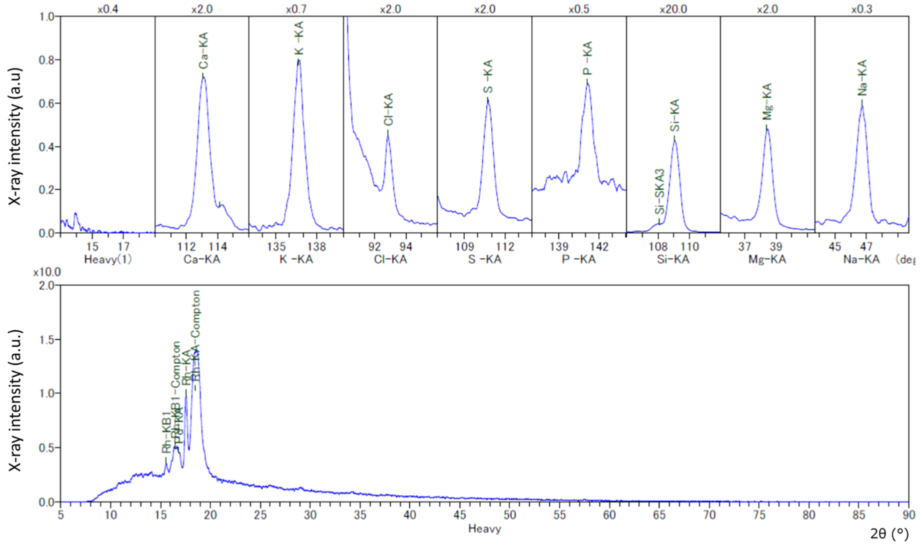


Fig. 6. Qualitative analysis chart of the drinking water (company C).

Table 5. SQX analysis results.

Unit: ppb

Component	Na	Mg	Si	P	S	Cl	K	Ca
SQX analysis value	4.8	8.0	13.6	0.11	1.1	1.6	3.4	8.5
Analysis value by calibration method	3.39	10.4	13.1	0.12	1.38	1.85	3.39	8.54

charts obtained using UltraCarry Light. The peaks of trace amount elements can be clearly observed.

Table 5 shows the SQX analysis results. For comparison, the results of quantitative analyses by the calibration method are shown in the lower line. The SQX analysis results are comparable to those of the calibration curve method, indicating that the SQX analysis is good for screening analysis of sub-ppm level trace elements.

5. Summary

UltraCarry has realized elemental analysis of several tens of ppb-level in waters. The sensitivities (lower limits of detection) were improved by more than 10 times compared with the conventional liquid sample cell method and filter paper method using MicroCarry.

Since sample preparation is simple, requiring only pipetting, personal error in analysis can be minimized. X-ray fluorescence analysis is a non-contact analysis method. Even if a sample contains high concentrations of an element, contamination of the instrument by the element does not occur, unlike other analytical methods. This is another advantage of this method.

In this paper, the analyses of mineral components in mineral waters using UltraCarry Light were described. Mineral components such as Ca, Mg, and Na were analyzed with high sensitivity and accuracy. Standardless SQX (Scan Quant X) analysis results gave almost the same results as the results with the calibration method.

In the environmental analysis field, extracted water is analyzed when investigating the elution amount of contaminated soil. Analysis of a solution extracted from contaminated soil using UltraCarry(8) was reported. In addition, the combination of UltraCarry and Rigaku's Cartesian geometry energy dispersive X-ray fluorescence spectrometer NEX CG, which has flexibility in utility and installation, has been applied to environmental analysis.

In the droplet method, some elements may volatilize when the sample is dried to remove the solvent. By dropping a retention agent on an UltraCarry along with a sample, these elements can be retained and quantitative analysis error can be prevented(9). In some cases, the dried sample is heterogeneously distributed on the filter paper. In this case, the internal standard method, in which a certain amount of an element having a wavelength (energy) close to the characteristic X-rays of the analytical line is added when dropping, is effective.

UltraCarry is a novel application tool that enables ppb-level trace analysis in X-ray fluorescence analysis. It can be expected to be utilized more in the environmental analysis field and other various fields.

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